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REMOTE FIBER OPTIC SENSOR FOR GASEOUS
AND LIQUID ENVIRONMENTS - PHASE II

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The goal of this program was to develop techniques and instrumentation for the implementation of Raman spectroscopy as a chemical sensor for both gas and liquid phase samples. Surface enhanced Raman techniques have been employed for low level detection. Novel SERS substrates have been demonstrated which enable complexation and preconcentration of gas phase species, a new development since SERS had previously been associated only with the liquid phase. The substrates were demonstrated for Raman sensing of hydrazine, ethanol, dimethyl methylphosphonate (DMMP), and other vapor species. In order to conduct remote sensing using Raman, a fiber optic probe was developed. The probe permits the excitation and collection of Raman spectra over >50 m of optical fiber without interference from scattering originating within the fibers themselves, previously a serious problem with this approach. Spectral analysis has been conducted with small spectrographs, some of them palm-sized. Special Raman filters based on holographic optical elements were developed for this purpose, removing all vestiges of the primary Raman excitation light before introducing the scattered Raman light into the spectrograph. Several spectrograph configurations were examined, including a novel Echelle design which enables better than 1 cm⁻¹ spectral resolution in a compact package (e.g., ~10³ cm⁻¹, including CCD detector).

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SUMMARY

The goal of this program was to develop techniques and instrumentation for the implementation of Raman spectroscopy as a chemical sensor for both gas and liquid phase samples. Surface enhanced Raman (SERS) techniques have been employed for low level detection. Fiber optically coupled probes and small spectrographs were developed to enable field deployment of Raman for chemical sensing in the environment.

Investigation of SERS Substrates

SERS has been associated previously with the liquid phase. Normally, SERS substrates comprising roughened Ag or Au are not reported to adsorb foreign species present in the gas phase. In order to detect SERS in the gas phase, a general screening of substrates for gas phase SERS activity was conducted. Substrates including Cu, CuO, Ag, AgO, Au, Au_2O_3 , Ni, Pd_2O_3 , Pd, PdO , Ir and IrO_2 were examined in air containing 0.5 to 50 ppm hydrazine and, to a lesser extent, other vapors. The substrates were roughened and oxidized using the general electrochemical techniques described in the Phase I Final Report. The substrates were examined with excitation wavelengths of 575 and 625 nm.

AgO and IrO_2 were both shown to be active SERS substrates for hydrazine present in air down to the sub parts per million level. The other substrates showed no SER spectra for hydrazine. In the SER spectrum of hydrazine on AgO , the intense bands at 935 cm^{-1} results from the N-N stretching vibration. The position is characteristic of unidentate hydrazine coordination on the AgO substrate. The bands between $1000 - 1600 \text{ cm}^{-1}$ are due to the N-H₂ bending, twisting and wagging vibrations. The bands in the $2800 - 3300 \text{ cm}^{-1}$ region correspond to the symmetric and antisymmetric N-H₂ stretching vibrations. For comparison, the gas phase Raman spectrum (unenhanced) of hydrazine has strong bands in the 1000 cm^{-1} region due to the N-N stretching vibration. The bands in the 3300 cm^{-1} region are due to the symmetric and antisymmetric N-H₂ stretching vibrations.

In the SER spectrum of hydrazine on IrO_2 , the N-N stretching vibration is shifted to 981 cm^{-1} , suggesting that the hydrazine is coordinated in a bridging mode. The N-H₂ bending, twisting and wagging vibrations appear as weak bands in the $1000 - 1100 \text{ cm}^{-1}$ region. The absorptions at 452 and 620 cm^{-1} are attributed to the NH umbrella mode. The down field spectrum was not recorded.

Hydrazine adsorption on AgO was demonstrated to be nearly reversible at ambient temperature. The intensity of the SERS signal on a AgO substrate changes as linearly the concentration is varied over the 0 to ~100 ppm. Multiple cycles between 0 and 5 ppm hydrazine exposure were conducted in a preliminary investigation of reversibility. The signal does not completely disappear, indicating that either a low concentration of hydrazine remains in the sample gas or that adsorption process is partially irreversible at some sites. In contrast, preliminary measurements indicate the adsorption of IrO_2 is irreversible at ambient temperature. The difference in the reversibility of the hydrazine adsorption on the two substrates probably reflects different bonding modes (i.e., unidentate versus bridging) as indicated by the SER spectra.

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The results on the oxide surfaces were extended to include the general idea of a substrate and apparatus for qualitatively and quantitatively detecting constituents of an environment by surface enhanced Raman spectroscopy (patent pending). The substrate is composed of two separate phases: an adsorbing phase which has an affinity for the molecular constituents of interest, and a metallic phase that possesses the specific geometry, chemical and electromagnetic properties required to enhance emission of Raman signal frequencies of adsorbed molecules. The apparatus incorporating these "engineered" substrates includes a monochromatic light source, a means to transmit the desired wavelength from the light source to the surface substrate surface, a means to collect the scattered Raman signal frequencies and transmit them to a detector, and a means to analyze the recorded response. Based on this approach, specific Raman detectors for vapor phase ethanol, formaldehyde, dimethyl methylphosphonate (DMMP) and NO₂ were demonstrated.

SERS/Raman Probes

One of overall objectives of the Phase II program was the development of a fiber optic based detection system for remote analysis. The results obtained on this program have indicated that the incorporation of long length (>50 m) fiber optics to Raman sampling is not a simple task. Background signals generated by the intense laser in the fiber optics can completely mask the signal for the compound of interest. The focus of the probe work has been the design and development of a fiber optically coupled probe assembly useful for both normal Raman and for SERS.

Several optical configurations were designed and tested which permitted the construction of a small probe which could be used for point measurements. It should be noted that in order to extend the sampling to a distance of 50 meters, there must be complete rejection of the laser (Rayleigh) line from reaching the collection fiber. A small amount (1 microwatt) of collected Rayleigh scattering will induce enough background signal in the collection fiber to completely mask the signal. Thus, the designs have incorporated multiple filter methodology. The initial "breadboarding" of the designs on the optical table have indicated that the filtering method has added a significant improvement in the collection of high quality Raman signals. We have also successfully incorporated smaller diameter fiber optics into the designs. Several advantages of smaller diameter fiber optics are: 1) a decreased level of silica Raman scattering due to smaller optical path, 2) better coupling into our Raman spectrometer, and 3) lower cost.

A patent has been issued for the fiber optic Raman probes developed on this program, for measuring Raman spectra of samples remote from the light source and detector. The probe head contains optical components which selectively remove unwanted fluorescence and Raman scattering arising within the input optical fiber. The optics also collect the Raman spectrum from the sample and provide the function of removing the primary Raman excitation line and directing the Raman spectrum into a second optical fiber which returns to the spectrograph. The optical components are disposed in a pen-like probe with parallel input and output fibers at one end and a sampling port at the other end. The sampling end can be fitted with various attachments, such as heaters and electrochemical microcells for conducting SERS.

Instrumentation

Three wavelength regions were evaluated for the compact Raman instrumentation. The wavelength regions are 500-540 nm, 750-800 nm and 1060-1100 nm. Each of these regions has advantages depending on the SERS substrates. Thus, the spectrometer for the compact SERS system should be capable of operation in all of the region with only minor changes. Two designs were investigated. The first is a Czerny-Turner spectrograph with a flat field of dispersion. The other design is a Echelle spectrometer, which utilizes a 2-D detector. The Echelle system provides the highest degree of resolution in a small compact design. Detection schemes will be based both on Hadamard transform techniques and on charge coupled devices were evaluated. The Hadamard technique can cost effectively emulate very expensive diode array and CCD detectors.

An enabling technology for implementing Raman techniques in small single stage monochrometers and even in filter-based instrumentation was demonstrated during this program: the holographic Bragg diffraction filter. The HBD filter is produced by recording a hologram in a dichromate gelatin/polymer graft emulsion approximately 20 μm thick between glass plates, producing narrow band rejection filters that can be fabricated anywhere in the 300-3000 nm wavelength range. The filters have a sharp rise from an optical density of <0.1 to ~6, thus allowing the effective filtering of the laser frequency used in Raman excitation from the comparatively weak Raman spectrum. Using these filters at the front end and CCD detection, Raman spectra were recorded using a simple, inexpensive 0.125 mm spectrograph down to $\sim 200 \text{ cm}^{-1}$ of the laser line, sufficient to capture the entire fingerprint region of most samples. Based on this work, Raman HBD filters are being sold commercially by several vendors of holographic optical components.

OTHERS ON PROJECT

Dr. R. David Rauh, Program Manager
Dr. Kevin M. Spencer, Senior Scientist
Mr. Robert B. Edmonds, Staff Scientist

PUBLICATIONS/PRESENTATIONS

"Chemical Sensor for Liquid Environments Based on Surface Enhanced Raman Spectroscopy," Abstract 168, 14th FACSS Meeting, Detroit, MI, October 1987.

"Fiber Optic Surface Enhanced Raman Chemical Sensors," The 174th Meeting of the Electrochemical Society, Abstract 662, Chicago, IL, October 9, 1988.

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"Fiber Optic Surface Enhanced Raman Spectroscopy for Environmental Monitoring," Abstract 443, 16th FACSS Meeting, Chicago, IL, October 1989.

"The Prospect of Utilizing Surface Enhanced Raman Spectroscopy (SERS) for Bio- and Biomedical Sensing," SPIE Biomedical Optics '90, Vol. 1201, Invited Paper pg. 438 (1990).

"Advances in Compact Raman Instrumentation," Abstract 420, 17th FACSS Meeting, Cleveland, OH, October 1990.

"The Utilization of Holographic Bragg Diffraction Filters for Rayleigh Line Rejection in Raman Spectroscopy", Applied Spectroscopy, **44**, 1558 (1990).

"Compact Raman Instrumentation for Process and Environmental Monitoring", submitted to SPIE OE/LASE'91 - Laser Spectroscopy , Vol. 1434, (1991).

Patents

"Apparatus for Measuring Raman Spectra Over Optical Fibers", U.S. Patent 5,112,127, May 15, 1992.

"Substrate and Apparatus for Surface Enhanced Raman Spectroscopy", U.S. Patent Application 07/621,172, filed November 30, 1990.

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